







Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative

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Integran Technologies Inc.





ASETS Defense Workshop
Sustainable Surface Engineering for Aerospace & Defense
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Report Documentation Page

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Hard Chrome Plating

(Why do we use it?)



Why Chrome plating?

Engineering hard chrome (EHC) coatings are used extensively in both industry and military applications due to their excellent performance characteristics.

- Wear
- Corrosion Resistance
- Dimensional Restoration

Where is Chrome Plating Used?

- Manufacturing and repair
- Dynamic components
- Hydraulic actuators
- Propeller hubs
- Engines
- Landing Gear





Hard Chrome Plating (The Problem)

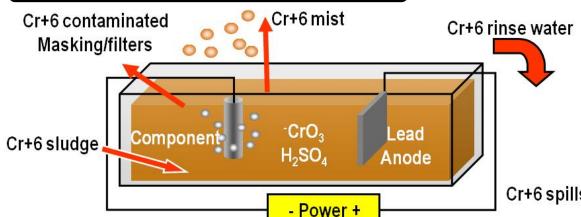


Hard Chrome Plating Environmental & Health Hazards

- Hard chrome plating utilizes chromium in the hexavalent state (Cr⁶⁺)
- Cr⁶⁺ is a known carcinogen and poses a health risk to operators
- OSHA lowered the Cr⁶⁺ PEL from 52 μg/m³ to 5 μg/m³

8 Apr 09, Memorandum, DoD Directive

- Hexavalent Chromium Management Policy
- NAVAIR Cr⁶⁺ Authorization Process





Cr+6 spills, leakage



Hard Chrome Alternative





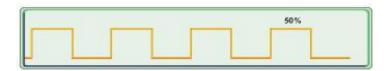
INTEGRAN Nanovate CR





Coating applied by electrodeposition

- Pulsed Current Waveform Engineering
 - Frequency (Hz) = $1/(t_{on}+t_{off})$
 - Duty Cycle (%) = $t_{on}/(t_{on}+t_{off})x100$



Electrodeposited nanocrystalline materials

- Favors nucleation of new grains over growth
- Results in an ultra-fine grain structure
- Uniform throughout thickness

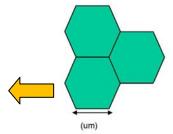
Leads to unique properties

- ↑ Yield Strength, wear, ultimate tensile strength
- ↑ Density
- ↓ Coefficient of friction

(Smaller grain size impedes dislocation movement and increases yield strength)

Hard Chrome Deposit



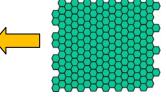


Polycrystalline (10-100 µm)

Cross section of typical EHC deposit showing macro cracks. Average grain sizes of $10 - 100 \mu m$.

*Nanovate™ CR





Nanocrystalline (< 100 nm)

Cross section of Nanovate™ CR deposit. Process creates electrodeposits with grains of 20 nm or less (1000 times smaller).

*Nanocrystalline Co-P Deposit



Hard Chrome Alternative

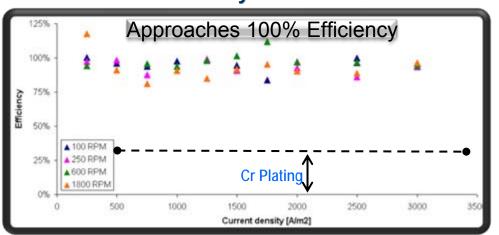




Process Comparison

	Nanovate [™] CR	EHC
Deposition Method	Electrodeposition (Pulse)	Electrodeposition (DC)
Part Geometries	LOS and NLOS	LOS and NLOS
Efficiency	85-95%	15-35%
Deposition Rate	0.002"-0.008" /hr	0.0005"-0.001" /hr
Emission Analysis	*Below OSHA limits	Cr+6

Cathode Efficiency





NanovateTM CR Plating Tank at FRCSE

- Up to 8X faster than Chrome plating
- Increased throughput
- One Nanovate CR tank can replace several EHC tanks
- More efficient (~ 90% Reduced power consumption)
- · Bath is Stable

*Co PEL is 20 µg/m3



Technology Development



- Developed and demonstrated at the lab scale
- Scaled up to industrial production & moved to DoD depot
- US Patents 5,433,797, 5,352,266, 7,320,832, 7,553,553 **STCP WP-0936 NESDI 348** INTEGRAN ITI Prototyping Line SERDP PP-1152 **©ESTCP** WP-0411 A FRC-SE Dem/Val Line 2000 2004 2010 2002 2006 2008 TRL 7 **TRL 1-4** TRL 5-6 P&WC Dem/val Line TPC 710 - 492064 **Enduro Industries** 2008-A-1455 780-505205 **Pilot Line**



Technology Dem/Val Site

(Full Operating Capability)



CIP # 0466

■ NAVAIR Fleet Readiness Center Jacksonville

- Dem/Val line in operation since 2006
- 250 gallon Plating Tank
- Pulse Power supply (1500A Peak Current)
- Activation tank used for most all alloys



Dem/Val Plating Tank



Power Supply



Remote Controller



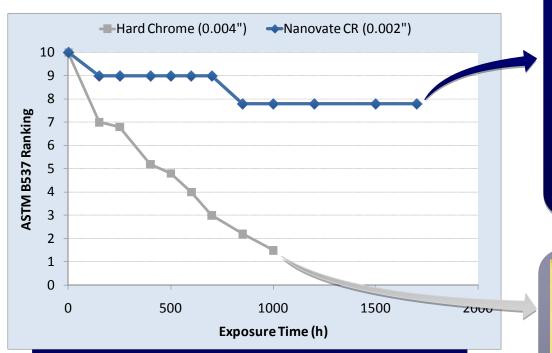
Acid/Fluoride Activation tank



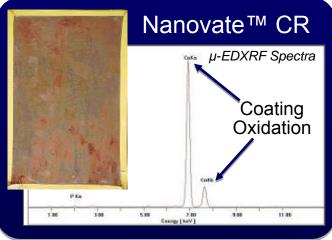
Corrosion Properties



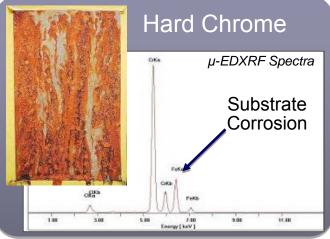




ASTM B537 Ranking following ASTM B117 Salt Spray



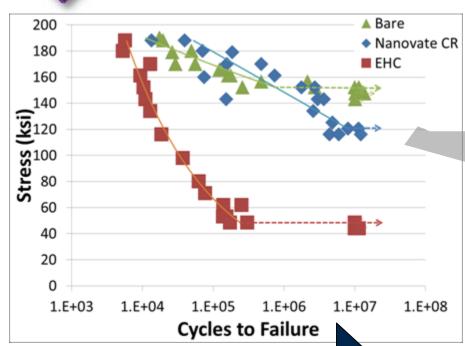
* Photos shown following 165 hrs





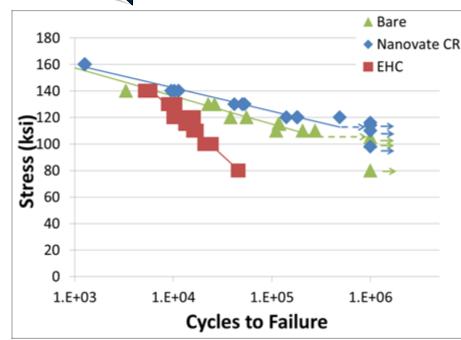
Fatigue Properties





Axial Fatigue (R=-1)
4340 substrate (UTS: 180-200 ksi)
Significant credit vs. EHC
Credit vs bare

Rotating Beam Fatigue 4340 substrate (UTS: 260-280 ksi) Significant credit vs. EHC Comparable to bare



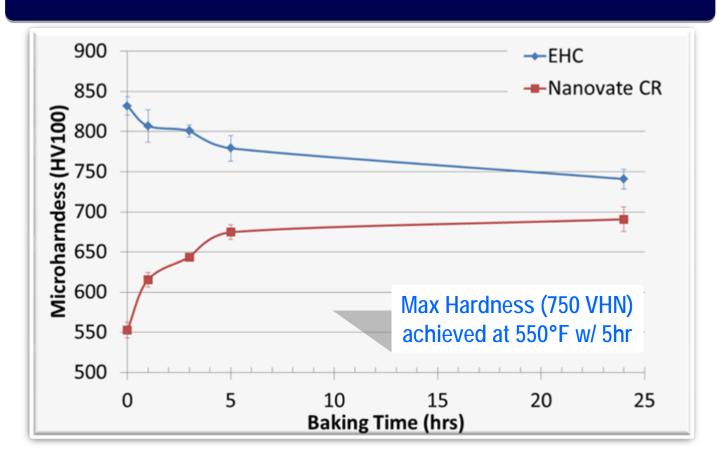


Hardness Properties





Nanovate CR hardness comparable to EHC after annealing at standard conditions for hydrogen embrittlement bakeout (375°F)





Technical Progress

(Masking Evaluation)



- Maskants evaluated and downselected
 - Enthone: Enplate Stop Off No. 1
 - Tolber: Microshield
- No adverse effects on bath or deposit quality
- Demonstrated on T45 pivot component







T-45 pivot shown with Enthone Maskant

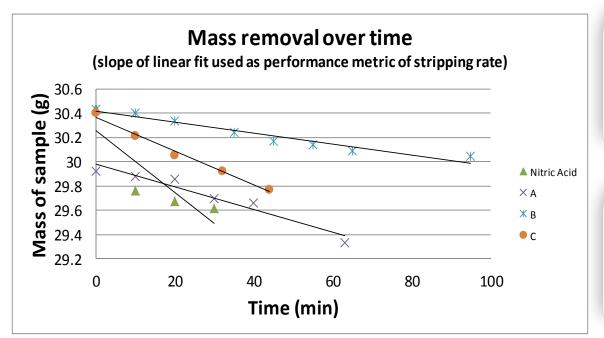


Technical Progress

(Coating Removal Evaluation)



- Strippants evaluated and downselected
 - (3) nitro-organic oxidizers with amino compounds
- 0.001"-0.004"/hr removal rates
- MacDermid METEX SCB Electroless Nickel Stripper was tested at JAX successfully.





Pre-plate coupon



Plated coupon



Stripped coupon



Technology Dem/Val at JAX (JTP Progress)



WP-0936 - Feb 2011



ESTCP JTP & Dem/Plan

24 Core Tests Defined in JTP

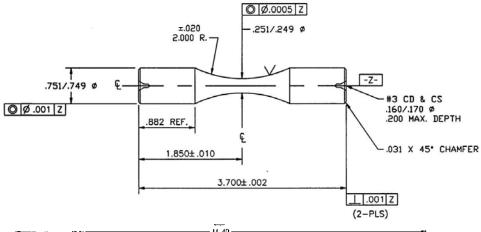
- Coating Quality
 - Appearance, Thickness, Porosity, Hardness, Grain size
- Ductility
- Stress (internal)
- Fatigue (Axial)
- Corrosion (B117, SO₂, Beach.OCP)
- Adhesion
- HE, HRE
- Fluid Compatibility
- Wear
 - (Taber, PoD, Rig, Falex, Gravelometry, SATEC)

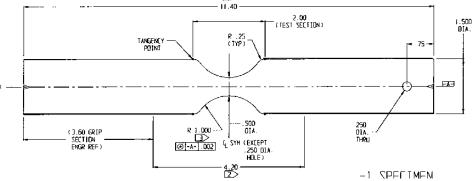


Fatigue/Wear Testing



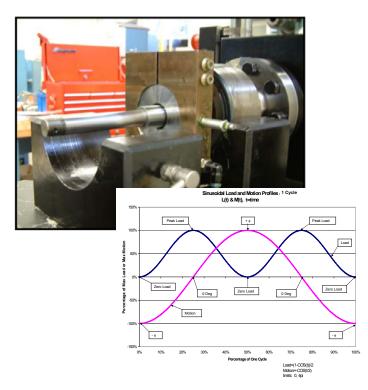






Axial Fatigue Test

- 4340 steel (260-280 ksi)
- Shot peened
- R ratio: R = -1



SATEC Oscillating Load Test

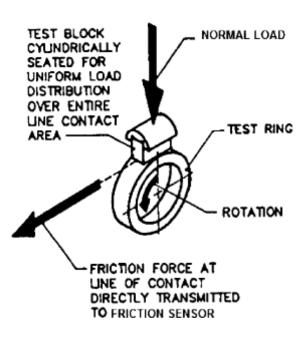
- Boeing Specific Test
- Pin/Bushing Oscillating Wear Test
- Constant/ Sinusoidal load-motion profile

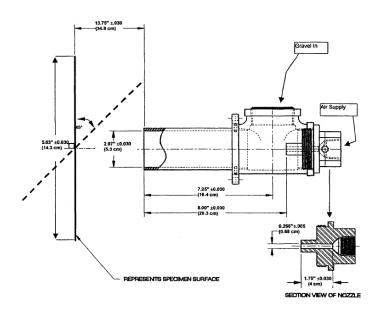


Wear Testing









FALEX Block on Ring

- Test per ASTM G77
- determines the resistance of materials to sliding wear
- Different Alloy/Coatings against Ring

Gravelometry

- Test per ASTM D3170
- Specimens mounted perpendicular to projected path
- Pea size gravel; air pressure 70 psi

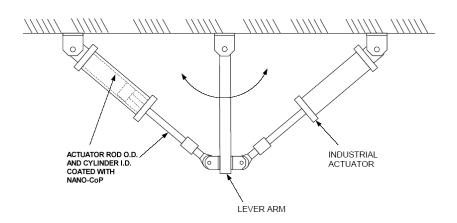


Endurance Rig Testing





- Assess wear performance vs. chrome as an ID actuator
- **Test developed by Messier-Dowty**
 - 20,000 Cycles
 - Observe the effect of surface finish, seal types, and hardening condition



Endurance Test Rig Schematic

lest Matrix*					
Surface Finish (Microinches)	Piston Seal	Rod Seal			
12-16					
4-6					
12-16					
4-6					
12-16					
4-6	Buna MTaa Saal	Buna-NTee Seal			
		Nitrile Butadiene			
12-16		Rubber			
	Kubber	Kubber			
4-6					
12-16	Viton Tee Seal	Viton Tee Seal			
12-16	Synthetic Rubber	Synthetic Rubber			
	Fluoropolymer	Fluoropolymer			
	Elastomer	Elastomer			
12-16					
12-16	PTFECap	Spring Energized			
	z z z cup	PTFE			
12-16	Buna-NO-	Buna-NO-			
10.16	Ring/Back-up-	Ring/Back-up-			
12-16	Nitrile Butadiene	Nitrile Butadiene			
		RubberO-Ring			
	Surface Finish (Microinches) 12-16 4-6 12-16 4-6 12-16 4-6 12-16 4-6 12-16 12-16 12-16 12-16 12-16	Piston Seal Piston Seal			

*In kind funding (Messier-Dowty)



Dem/Val Components T-45 Pivot Assembly

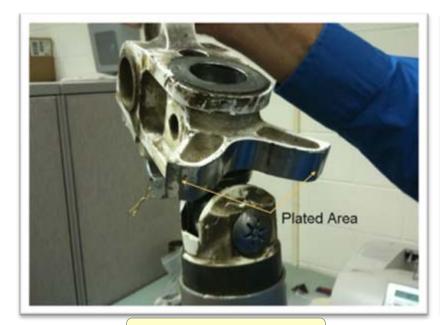


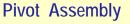


NAVAIR JAX Dem/Val for Air Vehicle Components

T-45 Arresting Hook Pivot Assembly





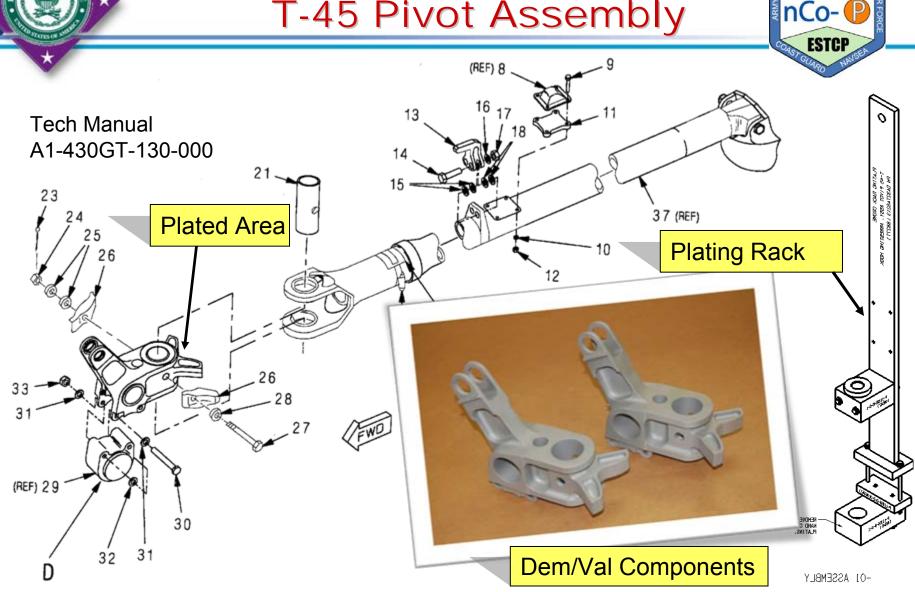




T-45 Goshawk Trainer Aircraft



Dem/Val Components T-45 Pivot Assembly





Electroplating Simulation: T-45 Pivot Assembly

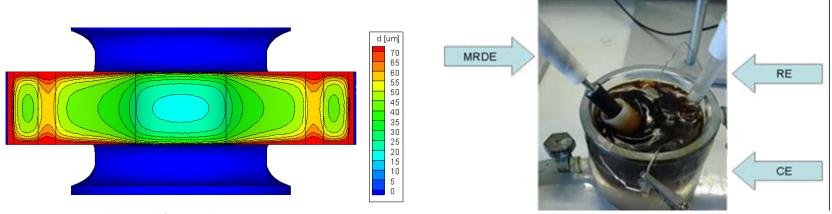




Electrochemical Modeling



- Conducted chemical characterization for model input
- Optimize current density distribution
- Control composition of electroplate
- Optimize coating properties
- Applied simulation to a complex geometry T45 Pivot Assembly



T-45 Pivot Assy

Bath Characterization



Potential Dem/Val Component Lifting Arm Pin





NAVAIR Lakehurst – Lifting Arm Pin

- Spotting Dolly- Lifting Arm Axel Pin
- EHC vs. Nanovate Cr vs. E-Ni





Various Lifting Pin Systems



Spotting Dolly Lifting Arm



NAVSEA Leveraged Effort LVS Hydraulic Cylinder





NAVSEA (NESDI & OSD Leveraged Effort)





- Marine Corps MK48
 LVS (Logistic Vehicle
 System) Hydraulic Cylinders
- (1) Evaluate coatings on steel and carburized steel laboratory panels
- (2) Evaluate optimum coatings with accelerated corrosion testing (GM9540P)
- (3) Field test on MK48 vehicles

Goals:

- Develop selection criteria for implementation into system repair / rebuild and spare parts sourcing
- Reduce corrosion maintenance requirements and repair costs of vehicles





NAVSEA Leveraged Effort LVS Hydraulic Cylinder



- Phase I: (*Carburized 1018 Steel Coupons)
 - Unofficial test results
 - ASTM B117 (passed)
 - ASTM F1978 Taber Abrasion (passed)
 - ASTM B571 Impact, Chisel/Knife, Peel (passed)





Taber abrasion

Impact/Adhesion

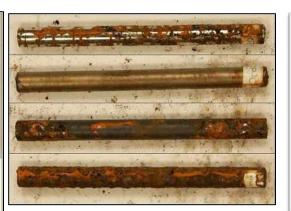




Corrosion

Corrosion

Cr nCoP X



Rig Test



Nanovate™ CR (center)

0 Hrs

480 Hrs

Y



Component Producibility

NAVSEA Refueling Parts



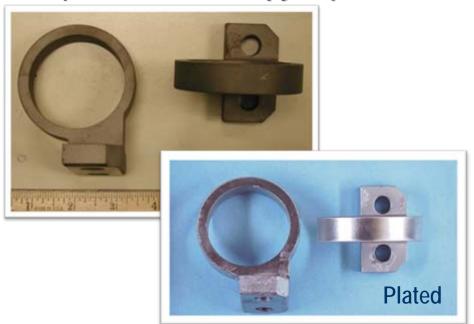






NAVSEA – NESDI Leveraged Effort

Refueling At Sea Components (Norfolk Naval Shipyard)



4340 Steel Bearing Housings





17-4 PH Stainless Roller Shafts



Component Producibility

Boeing Aircraft Parts





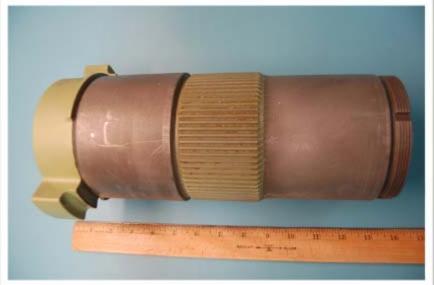
Boeing Seattle – Aircraft Components



Boeing Producibility Items







787 Drive Shaft – 4340M



Component Producibility

Landing Gear





Messier Dowty – V-22 Components



Messier-Dowty Producibility Items



V-22 NLG Piston



V-22 Osprey



Commercial Uses Prototyping & Development



■ Integran Technologies, Inc. (Toronto Canada)



- Nanovate CR prototyping line in operation since 2004
- 600 gallon Plating Tank
- In-line activation tanks
 - Mild steel, alloy steels, stainless steels, aluminum, Inconel, nickel...
- JTP sample production
- Commercial prototyping
 - Hydraulics, valves, pistons, shocks, engines, actuators, landing gear...
 - OEM and R&O



600 gal Plating tank at Integran (2010)



Commercial Uses Enduro Industries, Inc.



■ Enduro Industries, Inc. (Hannibal, MO)

- Nanovate CR process line installed and in operation since 2008
- Applying Nanovate CR to mild and induction hardened steel bars for use in hydraulic actuators for fluid power
- 700 gallon Plating Tank
- Integran provides on-going support of line
- Milestone: 1,000,000 Amp-hrs of production plating











Commercial Uses P&WC



■ Pratt & Whitney Canada (Longueil, Canada)

- EHC replacement for R&O of engine components
- Retrofit equipment to convert to Nanovate[™] CR Dem/Val Process Line
- Process line in use since Nov 2010
- 250 gallon Plating Tank



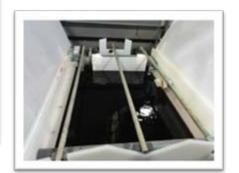






Support provided by:







Commercial Uses P&WC



Demonstration components plated for PT6 platform (shown after

machining):

Prop shaft

Seal runner



Seal runner plated at PWC (Jan 11)





Prop shaft plated at ITI (Oct 10)



Prop shaft plated at PWC (Jan 11)



Summary



■ Nanovate CR (nCo-P):

- Environmentally compliant EHC alternative
- Process compatible with existing plating infrastructure
- Reduced energy consumption, increased throughput
- Production process in commercial use (TRL 7)

Nanovate CR Material Properties

- Enhanced corrosion and wear
- Non-embrittling
- Improved fatigue performance vs. EHC

■ Future work (WP-0936)

- Performance testing (JTP)
- Dem/Val at NAVAIR JAX Depot
- OEM Producibility Components

For more information...





Visit our booth at ASETS Defense



Questions



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IH Assessment at NAVAIR JAX



NAVAIR-JAX IH assessment on Co emission on the Dem/Val tank.



DATE:	PERSONAL SAMPLING RESULTS (8-HR TWAS)	AREA SAMPLING RESULTS (8-HR TWAS)	VENTILATION MEASUREMENTS (TAKEN ON THE PULL SIDE)	DRY BULB READINGS (2)	RELATIVE HUMIDITY (3)
8 Aug 2007	Below the LOD	0.0023 mg/m ³	3519 FPM	Initial: 79.1°F Final: 97.3°F	Initial: 100% Final: 58%
9 Aug 2007	Below the LOD	0.0074 mg/m ³	3545 FPM	Initial: 81.2°F Final: 97.6°F	Initial: 100% Final: 58%
16 Aug 2007	Below the LOD	0.0017 mg/m ³	4001 FPM	Initial: 79.0°F Final: 94.4°F	Initial: 91% Final: 51%
22 Aug 2007	Below the LOD	Below the LOD	4366 FPM	Initial: 78.5°F Final: 95.0°F	Initial: 94% Final: 50%
24 Aug 2007	Below the LOD	Below the LOD	4088 FPM	Initial: 77.5°F Final: 94.2°F	Initial: 100% Final: 58%

Co PEL is 20 µg/m³





Dem/Val Component Spread Cylinder Hydraulic Rod





NAVAIR Lakehurst – Ground Support Equipment

- Spread Cylinder Hydraulic Rod (A/S32A-32 Aircraft Towing Tractor "Spotting Dolly")
- Supply System Risk







Spread Cylinder Rod in Assembly

Actuator Assembly

Two Different Sizes Shown



Coating Properties



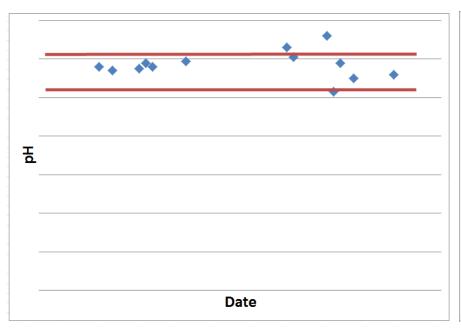
Nanovate ™ Z

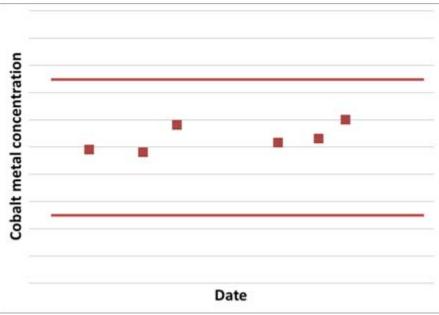
		Nanovate CR	EHC	
Appearance		Pit, Pore, Crack -free	Microcracked	
Duc	tility	2-7%	<1%	
	As-Deposited	530-600 VHN	Min. 600 VHN	
Hardness	Heat Treated	750 VHN	-	
A alla a alla a	Wear loss	6-7 x 10 ⁻⁶ mm ³ /Nm	9-11 x 10 ⁻⁶ mm ³ /Nm	
Adhesive Wear (Pin-on-disk)	Coefficient of friction	0.4-0.5	0.7	
	Pin Wear	Mild	Severe	
Corrosion †ASTM B537 Rating	Salt Spray ASTM B117	† Protection Rating 8 (1000 h) @ 0.002"	† Protection Rating 2 (1000 h) @ 0.004"	
Hydrogen Embrittlement	ASTM F519	Pass with bake	Pass with bake	
Fatigue	Axial & Rotating Beam	Credit vs. EHC Comparable to bare	Significant debit vs. bare	



Commercial Uses P&WC







- Technology transfer underway
- Integran provides on-going support for the line
- Early process monitoring demonstrates good production control

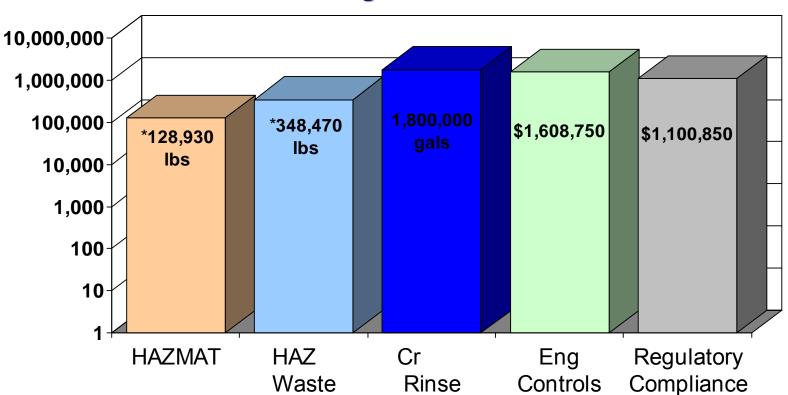


Environmental Driver/Benefit



(Hexavalent Chromium Plating at Navy FRCs)

Estimated NAVAIR P2 Savings over 10 Yrs



Note: the above projected savings are assumptions based on FRC-SE data extrapolated to other Navy FRCs

^{*} Estimated amounts due to chrome plating based on average Environmental Systems Allocation (ESA) data extrapolated across all FRCs over a 10 yr period





Cobalt Environment & Worker Safety



Cobalt Air Emissions – US EPA (Environmental Protection Agency)

- Emission limit different by state
 - Typical emission limit without requiring a license is 0.1 tons per year
- EPA estimating tool employed to determine emissions
 - Variables for estimator bath amps, bath operating hours
 - Typical results are less than 50 lbs (20kg) per year
 - Drivers size of parts being plated, number / shifts (amp hours)
- Nanovate CR emissions below limits

Aqueous System - Environmental

- Dust or fume not produced by the plating process
- Nano materials do not become airborne
 - Nano material plated directly onto the substrate material
 - No sprays to disperse nano materials in the atmosphere

Cobalt Development Institute – Additional Information

www.thecdi.com/cdi/images/documents/facts/Cobalt_Facts-HS&E.pdf

Highly Efficient Process Produces very little Cobalt emissions

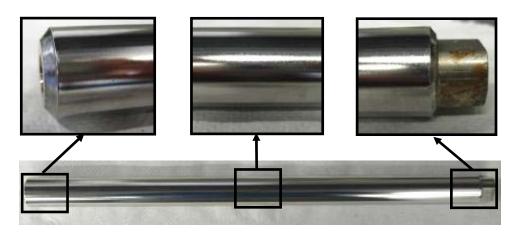




Rod-Seal Wear Testing



- Four PH 13-8Mo hydraulic actuator rods
 - Plated with 0.006-0.008" Nanovate CR
 - Hydrogen baked (375°F, 23h) or heat treated (300°C, 6 h)
 - Ground to 6-9 μinch, 12-16 μinch or superfinished to Ra < 4 μinch
- Testing conducted at NAVAIR-PAX
 - similar to ID cylinder wear wear against seals
 - Tests showed Nanovate CR comparable to EHC



Nanovate CR coated hydraulic rod

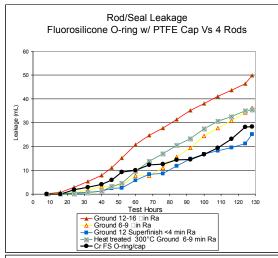


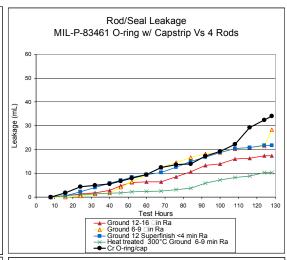
Rod-seal test apparatus

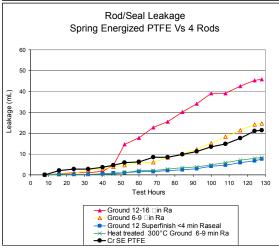


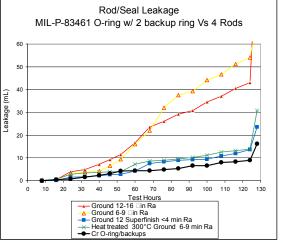
Rod-Seal Wear (Leakage, Various O-rings)











Black lines hard chrome from prior HCAT work

- Different test run
- Nanovate CR roughly comparable with hard chrome
- Ground surfaces higher leakage



Joint Test Protocol



	Sample Production Progress	Sample Completion	Test Completion
Material Characterization	50%	Feb 2011	Mar 2011
Adhesion	0%	Feb 2011	
Fluid Immersion	100%	Feb 2011	
Corrosion	50%		Apr 2011
Adhesive Wear (PoD, BoR)	50%		
Abrasive Wear	0%		Mar 2011
With support from Seal Wear	0%		
Gravelometry	0%		
Bushing Wear	0%		
Fatigue	0%		
Embrittlement	0%		